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Full Text

AN 2001:280710 CAPLUS

DN 134:319472

TI **Grinding** aids for use in silicone wafer **polishing** slurry containing colloidal **silica**

IN Mizutari, Takeaki; Komiya, Kaoru

PA Asahi Denka Kogyo K. K., Japan

SO Jpn. Kokai Tokkyo Koho, 6 pp.
CODEN: JKXXAF

DT Patent

LA Japanese

FAN.CNT 1

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI JP 2001110760	A2	20010420	JP 1999-282893	19991004
PRAI JP 1999-282893		19991004		

AB The **grinding** aids are of HO(PO)a(EO)b(PO)cH **block** copolymers (EO = **ethylene oxide**; PO = **propylene oxide**, a, b, c ≥1) which are included for improving the stability of **silica** dispersion.

1026-1-2
103-3
Mizutari et al

DERWENT-ACC-NO: 2001-505237

DERWENT-WEEK: 200202

TITLE: Polishing assistant for silicon wafer, consists of a block polyether

PATENT-ASSIGNEE: ASAHI DENKA KOGYO KK[ASAE]

PRIORITY-DATA: 1999JP-0282893 (October 4, 1999)

PATENT-FAMILY:

PUB-NO	PUB-DATE	LANGUAGE	PAGES	MAIN-IPC
JP 2001110760 A	April 20, 2001	N/A	006	H01L 021/304

APPLICATION-DATA:

PUB-NO	APPL-DESCRIPTOR	APPL-NO	APPL-DATE
JP2001110760A	N/A	1999JP-0282893	October 4, 1999

INT-CL (IPC): B24B037/00, B24B057/04 , C09K003/14 , H01L021/304

ABSTRACTED-PUB-NO: JP2001110760A

BASIC-ABSTRACT:

NOVELTY - A polishing assistant for a silicon wafer consists of a block polyether.

DETAILED DESCRIPTION - The block polyether of formula (1).

HO-(EO)d-(PO)e-(EO)f-H (1)

EO = oxyethylene;

PO = oxypropylene;

a, b, c = 1 or greater.

USE - The polishing assistant is suitably used for mirror surface polishing for the silicon wafer in production processes for a semiconductor.

ADVANTAGE - The polishing assistant yields an abrasive solution having superior polishing performance.

CHOSEN-DRAWING: Dwg.0/0

TITLE-TERMS: POLISH ASSIST SILICON WAFER CONSIST BLOCK POLYETHER

DERWENT-CLASS: A25 A88 P61 U11

CPI-CODES: A05-H03; A05-H04; A12-E07C; A12-H;

EPI-CODES: U11-C06A1A;

ENHANCED-POLYMER-INDEXING: Polymer Index [1.1] 018 ; R00351 G1558 D01 D23 D22 D31 D42 D50 D73 D82 F47 ; R00370 G1558 D01 D11 D10 D23 D22 D31 D42 D50 D73 D83 F47 ; H0022 H0011 ; H0066 H0044 H0011 ; P0055 ; P0975*R P0964 F34 D01 D10

Polymer Index [1.2] 018 ; ND01 ; B9999 B5094 B4977 B4740 ; Q9999 Q6600 ; Q9999 Q9110 ; Q9999 Q7476 Q7330

SECONDARY-ACC-NO:

CPI Secondary Accession Numbers: C2001-151877

Non-CPI Secondary Accession Numbers: N2001-374880

PAT-NO: JP02001110760A
DOCUMENT-IDENTIFIER: JP 2001110760 A
TITLE: POLISHING ASSISTANT FOR SILICON WAFER

PUBN-DATE: April 20, 2001

INVENTOR-INFORMATION:

NAME	COUNTRY
MIZUTARI, TAKEAKI	N/A
KOMIYA, KAORU	N/A

ASSIGNEE-INFORMATION:

NAME	COUNTRY
ASAHI DENKA KOGYO KK	N/A

APPL-NO: JP11282893
APPL-DATE: October 4, 1999

INT-CL (IPC): H01L021/304 , B24B037/00 , B24B057/04 , C09K003/14

ABSTRACT:

PROBLEM TO BE SOLVED: To provide a higher-performance polishing liquid for a silicon wafer so as to meet the needs in the semiconductor industry where a higher accuracy and higher quality of silicon wafer is required accompanying its development.

SOLUTION: A polishing assistant for a silicon wafer consisting of block polyether expressed by the following general formula: HO-(PO)a-(EO)b-(PO)c-H (in the formula, EO expresses an oxyethylene group, and PO expresses an oxypropylene group, and a, b, and c express numbers of one or over), and a polishing agent composition for a silicon wafer including it are provided. Using this polishing assistant will produce polishing liquid which is more excellent in polishing performance such as surface flatness, polishing speed, etc., without haze occurring on the surface of the wafer.

(19)日本国特許庁（ＪＰ）　(12)公開特許公報（Ａ）　(11)特許出願公開番号
特開2001－110760
（P2001－110760A）
(43)公開日　平成13年４月20日(2001.4.20)

(51)Int.Cl.'		識別記号	FI		テーマコード'(参考)
H01L	21/304	622	H01L	21/304	622D　3C047
					622C　3C058
B24B	37/00		B24B	37/00	H
	57/04			57/04	
C09K	3/14	550	C09K	3/14	550D

審査請求　未請求　請求項の数7　OL　（全６頁）　最終頁に続く

(21)出願番号　特願平11－282893

(22)出願日　平成11年10月４日(1999.10.4)

(71)出願人　000000387
旭電化工業株式会社
東京都荒川区東尾久７丁目２番35号
(72)発明者　水足　岳明
東京都荒川区東尾久７丁目２番35号　旭電化工業株式会社内
(72)発明者　小宮　薫
東京都荒川区東尾久７丁目２番35号　旭電化工業株式会社内
(74)代理人　100057874
弁理士　曾我　道照　（外６名）

Ｆターム(参考)　3C047 GG00
3C058 AA07 CA04 CB02 CB03 CB10
DA02

(54)【発明の名称】　シリコンウェハー用研磨助剤

(57)【要約】
【課題】　半導体産業の発展に伴い、より高精度、高品質のシリコンウェハーが求められ、それに伴いより高性能のシリコンウェハー用の研磨液が求められている。
【解決手段】　本発明は、下記の一般式（１）

$$HO-(PO)_a-(EO)_b-(PO)_c-H \qquad (1)$$

（式中、ＥＯはオキシエチレン基を表わし、ＰＯはオキシプロピレン基を表わし、ａ、ｂ及びｃは１以上の数を表わす。）で表わされるブロック型ポリエーテルからなるシリコンウェハー用研磨助剤及びこれを含むシリコンウェハー用研磨剤組成物を提供する。本発明の研磨助剤を使用すると、ウェハー表面にヘイズが発生せず、表面の平坦さや研磨速度等の研磨性能のより優れた研磨液が得られる。

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【特許請求の範囲】

$$HO-(PO)_a-(EO)_b-(PO)_c-H \quad (1)$$

（式中、EOはオキシエチレン基を表わし、POはオキシプロピレン基を表わし、a、b及びcは1以上の数を表わす。）で表わされるブロック型ポリエーテルからなるシリコンウェハー用研磨助剤。

【請求項2】　一般式（1）で表わされるブロック型ポリエーテルの分子量が、1，000～10，000であ※

$$HO-(EO)_d-(PO)_e-(EO)_f-H \quad (2)$$

（式中、EOはオキシエチレン基を表わし、POはオキシプロピレン基を表わし、d、e及びfは1以上の数を表わす。）で表わされるブロック型ポリエーテルを含有する請求項1乃至3の何れか1項に記載のシリコンウェハー用研磨助剤。

【請求項5】　請求項1乃至4の何れか1項に記載のシリコンウェハー用研磨助剤及びコロイダルシリカを含むシリコンウェハー用研磨剤組成物。

【請求項6】　請求項5に記載のシリコンウェハー用研磨剤組成物を用いるシリコンウェハーの研磨方法。

【請求項7】　請求項6に記載のシリコンウェハーの研磨方法により研磨されたシリコンウェハー。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、半導体の製造工程でのシリコンウェハーの鏡面研磨に好適に使用されるシリコンウェハー用研磨助剤に関する。

【0002】

【従来の技術】半導体用シリコンウェハーの鏡面研磨工程には、シリコンインゴットから切断によって、シリコンをウェハー状に切り出した際に生じる切断歪層及び表面うねりを除去するラッピング工程（粗研磨）と、ラッピング工程を経たラップドシリコンウェハーを、目的とする表面精度に仕上げるポリッシング工程（精密研磨工程）がある。又、後者のポリッシング工程には、大体の精度に仕上げる1次ポリッシング工程（1次研磨工程）と、目的とする表面精度に仕上げるファイナルポリッシング工程（最終研磨工程）に分別され、場合によっては1次ポリッシング工程を2つに分け、1次、2次ポリッシング工程と称する場合もある。従来、シリコンウェハーの研磨剤としてはコロイダルシリカや酸化セリウムが一般的に使用されてきた。しかし、コロイダルシリカ研磨液や酸化セリウム研磨液のみを用いて研磨を行うと、★

$$HO-(PO)_a-(EO)_b-(PO)_c-H \quad (1)$$

（式中、EOはオキシエチレン基を表わし、POはオキシプロピレン基を表わし、a、b及びcは1以上の数を表わす。）で表わされるブロック型ポリエーテルからなるシリコンウェハー用研磨助剤である。

【0005】

【発明の実施の形態】一般式（1）において、EOはオキシエチレン基を表わし、POはオキシプロピレン基を☆

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＊＊【請求項1】　下記の一般式（1）

※る請求項1に記載のシリコンウェハー用研磨助剤。

【請求項3】　一般式（1）中のEO及びPOの重量比が、EO：PO＝5：95～60：40であるブロック型ポリエーテルからなる請求項1又は2に記載のシリコンウェハー用研磨助剤。

【請求項4】　更に、下記の一般式（2）

★研磨工程終了時にシリコンウェハーの表面にヘイズ（曇り）が生じるという問題がある。又、パウダー状シリカを研磨剤として用いるとヘイズは発生しにくいが、パウダー状シリカを水溶液に均一に分散させる工程が新たに必要となり、更に、静置しておくとパウダー状シリカが沈殿するために常に研磨液を撹拌している必要があった。特開平2-125413号公報、特開昭61-209909号公報、特開昭61-209910号公報等には、コロイダルシリカを用いたシリコンウェハー研磨剤及び研磨方法の改良法が提案されているが、根本的な問題の解決にはなっていないのが現状であった。

【0003】

【発明が解決しようとする課題】これらの問題を解決すべく、従来から、コロイダルシリカ等のシリコン研磨液に添加する研磨助剤が検討されてきた。例えば、特開平4-291722号公報には、コロイダルシリカ及び特定のHLB値を示す非イオン界面活性剤を含むシリコンウェハー用研磨剤が開示されている。特開平4-291723号公報には、コロイダルシリカ及び特定のアニオン界面活性剤を含むシリコンウェハー用研磨剤が開示されている。これらの界面活性剤は、研磨液の表面張力を調整して、研磨時に研磨されるシリコンウェハーの研磨表面に研磨液を十分保持させるために使用されていた。しかし、半導体産業の発展の結果、より高精度、高品質のシリコンウェハーが求められるにつれ上述のような界面活性剤ではヘイズの防止はできるが研磨表面の平坦さや研磨速度等の研磨助剤としての性能が不十分であることが指摘されはじめた。

【0004】

【課題を解決するための手段】そこで本発明者らは鋭意検討し、特定の構造を有するポリエーテルが従来の研磨助剤より優れた性能を示すことを発見し本発明を完成させた。即ち、本発明は、下記の一般式（1）

☆表わす。a、b及びcは1以上の数を表わす。a、b及びcの好ましい値の範囲は、一般式（1）で表わされるブロック型ポリエーテルの分子量及びHLB等によって相関的に変化するので一概には言えないが、a＋c及びbはそれぞれ通常は2～500程度、更に好ましくは10～100程度である。一般式（1）で表わされるブロック型ポリエーテルは、エチレンオキサイドをbモル重

合させて得られたポリエチレングリコールに、プロピレンオキサイドをａ＋ｃモル付加させることにより得ることができる。この際、ベースとなるポリエチレングリコールの分子量や、付加させるプロピレンオキサイドの量等により、得られるブロック型ポリエーテルの物性、例えば、表面張力、親水性等を制御することができるので、研磨されるシリコンウェハーや研磨する方法に適したブロック型ポリエーテルを選択して使用することが可能である。

【０００６】又、一般式（１）で表わされるブロック型ポリエーテルの分子量は特に限定されないが、あまり小さすぎると、研磨液の表面張力を調整する効果等が不十分になり、あまり大きすぎると、一般式（１）で表わされるブロック型ポリエーテルの粘度が上昇しすぎるため、１，０００～１０，０００が好ましい。一般式（１）で表わされるブロック型ポリエーテルは、１種を単独で使用することは勿論、ａ、ｂ又はｃの値が異なる＊＊２種以上のブロック型ポリエーテルを使用することができ、研磨液の表面張力や親水性等を微調整したい場合は、２種以上を併用して使用することが好ましい。一般式（１）で表わされるブロック型ポリエーテルの中でも、シリコンウェハーを研磨する研磨液に特に好ましい表面張力を与えるものは、ＥＯ及びＰＯの重量比がＥＯ：ＰＯ＝５：９５～６０：４０であるブロック型ポリエーテルである。このようなブロック型ポリエーテルを使用した場合は、研磨液にシリコンウェハーを研磨するのに特に適した表面張力を与えることができるので、ヘイズが無く、研磨表面が平滑・平坦なシリコンウェハーを得ることができ、その結果高性能の半導体素子が得られる。

【０００７】更に、一般式（１）で表わされるブロック型ポリエーテルは、次の一般式（２）で表わされるブロック型ポリエーテルと併用することができる。

$$HO-(EO)_d-(PO)_e-(EO)_f-H \qquad (2)$$

一般式（２）において、ｄ、ｅ及びｆは１以上の数を表わす。ｄ、ｅ及びｆの好ましい値の範囲は、一般式（２）で表わされるブロック型ポリエーテルの分子量及びＨＬＢ等によって相関的に変化するので一概には言えないが、ｄ＋ｆ及びｅがそれぞれ通常は２～５００程度、更に好ましくは１０～１００程度である。一般式（２）で表わされるブロック型ポリエーテルは、プロピレンオキサイドをｅモル重合させて得られたポリプロピレングリコールに、エチレンオキサイドをｄ＋ｆモル付加させることにより得ることができる。

【０００８】又、一般式（１）で表わされるブロック型ポリエーテルに、更に、例えば、プロピレングリコール、エチレングリコール、ブタンジオール等のグリコール系溶剤を添加すると、研磨液の粘度を下げ、又、コロイダルシリカ等の水分散シリカの分散性を向上させるので好ましい。ブロック型ポリエーテルとグリコール系溶剤を併用する場合は、ブロック型ポリエーテルを、ブロック型ポリエーテルとグリコール系溶剤からなる組成物の全量に対して６０～９９重量％、グリコール系溶剤を組成物全量に対して１～４０重量％とすることが好ましい。

【０００９】上記の本発明のシリコンウェハー用研磨助剤は、通常、研磨剤である水分散シリカに添加して使用される。水分散シリカとしては、例えば、水分散パウダーシリカ、コロイダルシリカ等が挙げられるが、中でもｐＨ８～１２に調整されたアルカリ性コロイダルシリカが好ましい。アルカリ性コロイダルシリカの中でも、平※※均粒子径は７～１００μｍのものが好ましく、アルカリ性コロイダルシリカの濃度は２０～６０重量％が好ましい。

【００１０】本発明のシリコンウェハー用研磨助剤の添加量は特に限定されないが、水分散シリカの固形分に対して０．００５～５重量％添加することが好ましい。その他、本発明のシリコンウェハー研磨助剤は、メタノール、エタノール、２－プロパノール等の低級アルコール；メチルセロソルブ、エチルセロソルブ、ブチルセロソルブ、メチルカルビトール、エチルカルビトール、ブチルカルビトール等の低級アルコールのアルコキシレート；高級アルコールのアルキレンオキサイド付加物等の界面活性剤と併用することができる。本発明のシリコンウェハー研磨助剤は、シリコンウェハーのラッピング工程又はポリッシング工程の何れにも使用することができ、研磨液の表面張力を適切な値に調整することができるため、シリコンウェハー上にヘイズが無く、表面が平滑・平坦なシリコンウェハーを得ることができ、その結果高性能の半導体素子が得られる。

【００１１】

【実施例】以下、実施例により本発明を更に具体的に説明する。尚、以下の実施例中、％は特に記載が無い限り重量基準である。評価試験に用いた本発明の研磨助剤及び比較品は以下のとおりである。

【００１２】

【表１】

5　　6

表1

		ポリエーテル（A）			ポリエーテル（B）			プロピレングリコール (%)
		a+c	b	配合量 (%)	a+c	b	配合量 (%)	
本発明品	1	29	26	80	32	13	20	
	2	29	26	60	32	13	40	
	3	29	26	80	31	7	20	
	4	29	26	70	35	24	30	
	5	26	15	85	53	13	15	
	6	26	15	100				
	7	53	47	70	32	13	30	
	8	53	47	80	31	7	20	
	9	29	26	55	35	24	45	
	10	29	26	60	32	13	20	20
	11	17	15	70	32	13	30	

【0013】　　＊　＊【表2】

表2

		ポリエーテル（A）			ポリエーテル（C）			プロピレングリコール (%)
		a+c	b	配合量 (%)	d+f	e	配合量 (%)	
	12	29	26	70	9	34	30	
	13	32	13	20	33	37	60	20
	14	53	13	35	33	37	65	

【0014】※：表1及び表2において、ポリエーテル（A）及び（B）は一般式（1）で表わされるブロック型ポリエーテルであり、ポリエーテル（C）は一般式（2）で表わされるブロック型ポリエーテルである。

【0015】

比較品1　アルミン酸ナトリウム

比較品2　ラウリルスルホン酸ナトリウム

比較品3　ノニルフェノールエチレンオキサイド10モル付加物

比較品4　（ブランク）

【0016】（実施例1）コロイダルシリカとしてアデライトAT-30S（商品名、旭電化工業製、平均粒子径7～10μm、シリカ固形分30%）を用い、これを※水でシリカ固形分5．0%に希釈した。これに、前記本発明の研磨助剤及び比較品をシリカ固形分に対して0．1%（比較品1は1．0%）添加し、よく撹拌して均一化して希釈研磨液とした。これらの希釈研磨液を使用して、スライシングした4インチのシリコンウェハー100枚についてラッピング処理を行った。ラッピング処理後、100枚のシリコンウェハーについて、ウェハーの擦り傷、ウェハーの割れ、ウェハーの微小表面クラックの各不良項目に該当するものの枚数を数えた。その結果を表3に示す。

【0017】

【表3】

表3

	擦り傷（枚）	割れ（枚）	クラック（枚）
本発明品　1	0	0	0
本発明品　2	0	0	0
本発明品　3	1	0	0
本発明品　4	1	0	0
本発明品　5	1	0	0
本発明品　6	0	0	0
本発明品　7	0	0	0
本発明品　8	1	0	0
本発明品　9	0	0	0
本発明品１０	1	0	0
本発明品１１	1	0	0
本発明品１２	1	0	0
本発明品１３	1	0	0
本発明品１４	1	0	0
比較例　1	5	5	4
比較例　2	6	4	3
比較例　3	3	5	4
比較例　4	9	１０	１０

【００１８】（実施例２）コロイダルシリカとしてアデライトＡＴ－３０Ｓ（商品名、旭電化工業製、平均粒子径7～１０μｍ、シリカ固形分３０％）を用い、これを水でシリカ固形分５．０％に希釈した。これに本発明の研磨助剤及び比較品をシリカ固形分に対して０．１％（比較品1は１．０％）添加し、よく撹拌して均一化して希釈研磨液とした。この希釈研磨液を以下の条件でポリッシングマシーンに流し込み、1次ポリッシング工程を経た1次ポリッシングシリコンウェハーを研磨した。

【００１９】<条件>

ポリッシングマシーン：ＬＰＨ－１５改良機（ラップマスター製）

ポリッシング盤直径：１５インチ

加工圧力：１００ｇ／ｃｍ²

加工温度：３０℃

加工液供給量：１０リットル／時間

加工時間：１時間

加工枚数：１枚

ポリッシャー：ＳＵＰＲＥＭＥ　ＲＮ－Ｈ（ローデル・ニッタ製）

上記条件下でファイナルポリッシングを行い、終了後、ウェハー表面を乾燥させないように注意して過酸化水素＊ーアンモニア溶液で８０℃でＲＣＡ洗浄した。洗浄後、クイックダンプ洗浄を行い、スピンドライヤーで乾燥させた。乾燥後、以下の評価を行った。

【００２０】評価１：ヘイズの有無

グリーンベンチ内でハロゲン平行光（超高輝度検査用照明装置Ｕ１Ｈ－１Ｈ、インテック製）のウェハー表面からの反射を目視で観察し、ヘイズの発生を観察した。

評価２：表面粗さ

研磨ウェハーの表面粗さを光学干渉式粗さ計（ＷＹＫＯ　ＴＯＰＯ－３Ｄ、ＷＹＫＯ製、２５０μｍ）で平均2乗粗さを測定した。

評価３：平坦度

研磨ウェハーの表面平坦度、即ち研磨ウェハーの最大厚さと最小厚さの差（ＴＴＶ）を、ＴＴＶ測定装置（ＡＤＥマイクロスキャン８３００、ＡＤＥ製）により測定した。

評価４：研磨速度

研磨中のシリコンウェハーの研磨速度を研磨後のウェハーの膜厚減を７×７点測定し算出した。これらの評価結果を表4に示す。

【００２１】

【表４】

表4

	ヘイズ	表面粗さ (nm)	平坦度 (μm)	研磨速度 (μm/分)
本発明品 1	無し	0.15	0.39	2.4
本発明品 2	無し	0.22	0.38	2.9
本発明品 3	無し	0.24	0.55	3.3
本発明品 4	無し	0.28	0.44	1.9
本発明品 5	無し	0.30	0.41	2.5
本発明品 6	無し	0.17	0.52	2.2
本発明品 7	無し	0.22	0.33	3.0
本発明品 8	無し	0.29	0.32	3.4
本発明品 9	無し	0.20	0.60	3.0
本発明品10	無し	0.27	0.30	2.9
本発明品11	無し	0.25	0.27	2.7
本発明品12	無し	0.31	0.51	2.8
本発明品13	無し	0.42	0.46	3.5
本発明品14	無し	0.30	0.45	2.9
比較例 1	無し	0.88	1.42	0.8
比較例 2	無し	0.91	1.33	0.7
比較例 3	無し	0.94	1.34	0.9
比較例 4	無し	1.24	2.04	1.4

【0022】以上の実施例の各評価結果から、本発明の研磨助剤を使用した研磨液は、アニオン界面活性剤（比較品2）、非イオン界面活性剤（比較品3）を使用した研磨液に比べて、シリコンウェハーの割れや擦り傷がなく、表面粗さ、平坦度、研磨速度等に優れていることが＊分かる。

【0023】

【発明の効果】本発明の効果は、より研磨性能の優れた研磨液を与える新規なシリコンウェハー研磨助剤を提供したことにある。

フロントページの続き

(51)Int.Cl.⁷	識別記号	FI	テーマコード（参考）
C09K 3/14	550	C09K 3/14	550C

1026-(1-2)
103-(3,10)
JP 2001-110,760

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CLAIMS

[Claim(s)]
[Claim 1] The following general formula (1)
HO-(PO)a-(EO)b-(PO)c-H (1)
(EO expresses an oxyethylene radical among a formula, PO expresses an oxypropylene radical, and a, b, and c express one or more numbers.) The polish assistant for silicon wafers which consists of a block-type polyether expressed.
[Claim 2] The polish assistant for silicon wafers according to claim 1 whose molecular weight of the block-type polyether expressed with a general formula (1) is 1,000-10,000.
[Claim 3] The polish assistant for silicon wafers according to claim 1 or 2 which the weight ratio of EO and PO in a general formula (1) becomes from the block-type polyether which is EO:PO=5:95-60:40.
[Claim 4] Furthermore, the following general formula (2)
HO-(EO)d-(PO)e-(EO)f-H (2)
(-- EO expresses an oxyethylene radical among a formula, PO expresses an oxypropylene radical, and d, e, and f express one or more numbers.) -- polish assistant for silicon wafers given in claim 1 containing the block-type polyether expressed thru/or any 1 term of 3.
[Claim 5] The abrasive material constituent for silicon wafers which contains the polish assistant for silicon wafers and colloidal silica of a publication in claim 1 thru/or any 1 term of 4.
[Claim 6] The polish approach of the silicon wafer using the abrasive material constituent for silicon wafers according to claim 5.
[Claim 7] The silicon wafer ground by the polish approach of a silicon wafer according to claim 6.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the polish assistant for silicon wafers used suitable for mirror polishing of the silicon wafer in the production process of a semi-conductor.
[0002]
[Description of the Prior Art] There are a wrapping process (rough polish) which removes the cutting distorted layer and surface waviness which are produced when silicon is cut down in the shape of a wafer by cutting from a silicon ingot, and a polishing process (precision polish process) which makes the surface precision made into the purpose to lap DOSHIRIKONWEHA which passed through the wrapping process as mirror-polishing process of the silicon wafer for semi-conductors. Moreover, at the latter polishing process, it is classified by primary polishing processes (primary polish processes) to which a great portion of precision is made, and the final polishing process (the last polish process) to which the surface precision made into the purpose is made, and primary polishing processes may be called the primary secondary polishing processes by dividing into two depending on the case. Conventionally, generally as an abrasive material of a silicon wafer, colloidal silica and cerium oxide have been used. However, when it grinds only using colloidal silica polish liquid or cerium oxide polish liquid, there is a problem that Hayes (cloudiness) is generated on the surface of a silicon wafer, at the time of polish process termination. Moreover, when the powder-like silica was used as an abrasive material, it was hard to generate Hayes, but if the process which homogeneity is made to distribute was newly needed for a water solution and the powder-like silica was put further, in order that a powder-like silica might precipitate, polish liquid always needed to be stirred. Although the method of improving the silicon wafer abrasive material which used colloidal silica, and the polish approach was proposed by JP,2-125413,A, JP,61-209909,A, and JP,61-209910,A, the present condition was not being solution of a fundamental problem.
[0003]
[Problem(s) to be Solved by the Invention] The polish assistant added in silicon polish liquid, such as colloidal silica, has been examined from the former that these problems should be solved. For example, the abrasive material for silicon wafers containing the nonionic surface active agent which shows colloidal silica and a specific HLB value to a publication-number No. 291722 [four to] official report is indicated. The abrasive material for silicon wafers which contains colloidal silica and a specific anionic surface active agent in a publication-number No. 291723 [four to] official report is indicated. These surfactants adjusted the surface tension of polish liquid, and they were used in order to make polish liquid hold enough on the polish front face of the silicon wafer ground at the time of polish. However, as a result of development of semiconductor industry, although prevention of Hayes was completed, with the above surfactants, it began to be pointed out that the engine performance as polish assistants, such as flat [on the front face of polish] and a polish rate, is inadequate, as the silicon wafer of high degree of accuracy and high quality was called for more.
[0004]

[Means for Solving the Problem] Then, this invention persons inquire wholeheartedly, and the polyether which has specific structure discovered that the engine performance superior to the conventional polish assistant was shown, and completed this invention. That is, this invention is the following general formula (1).

HO-(PO)a-(EO)b-(PO)c-H (1)

(-- EO expresses an oxyethylene radical among a formula, PO expresses an oxypropylene radical, and a, b, and c express one or more numbers.) -- it is the polish assistant for silicon wafers which consists of a block-type polyether expressed.

[0005]

[Embodiment of the Invention] In a general formula (1), EO expresses an oxyethylene radical and PO expresses an oxypropylene radical. a, b, and c express one or more numbers. Although the range of the desirable value of a, b, and c does not generally have ****** since it changes with molecular weight, HLB, etc. of a block-type polyether which are expressed with a general formula (1) interrelatively, a+c and b are usually ten to about 100 still more preferably two to about 500, respectively. The block-type polyether expressed with a general formula (1) can be obtained by carrying out a+c mol addition of the propylene oxide to the polyethylene glycol which was made to carry out the b mol polymerization of the ethyleneoxide, and was obtained. Under the present circumstances, since the physical properties of the block-type polyether obtained, for example, surface tension, a hydrophilic property, etc. are controllable by the molecular weight of the polyethylene glycol used as the base, the amount of propylene oxide made to add, it is possible to use it, choosing the block-type polyether suitable for the silicon wafer ground or the approach of grinding.

[0006] Moreover, although especially the molecular weight of the block-type polyether expressed with a general formula (1) is not limited, if the effectiveness of adjusting the surface tension of polish liquid if too not much small etc. becomes inadequate and is too large not much, since the viscosity of the block-type polyether expressed with a general formula (1) will rise too much, 1,000-10,000 are desirable. Two or more sorts of block-type polyethers from which the value of a, b, or c differs can be used as well as using one sort independently, and, as for the block-type polyether expressed with a general formula (1), it is desirable to use together and use two or more sorts to tune surface tension, a hydrophilic property, etc. of polish liquid finely. Especially the thing that gives desirable surface tension to the polish liquid which grinds a silicon wafer also in the block-type polyether expressed with a general formula (1) is a block-type polyether whose weight ratio of EO and PO is EO:PO=5:95-60:40. Since the surface tension which was suitable for polish liquid especially grinding a silicon wafer can be given when such a block-type polyether is used, there is not Hayes, a silicon wafer smooth [a polish front face] and flat can be obtained, and, as a result, the semiconductor device of high performance is obtained.

[0007] Furthermore, the block-type polyether expressed with a general formula (1) can be used together with the block-type polyether expressed with the following general formula (2).

HO-(EO)d-(PO)e-(EO)f-H (2)

In a general formula (2), d, e, and f express one or more numbers. Although the range of the desirable value of d, e, and f does not generally have ****** since it changes with molecular weight, HLB, etc. of a block-type polyether which are expressed with a general formula (2) interrelatively, d+f and e are usually ten to about 100 still more preferably two to about 500, respectively. The block-type polyether expressed with a general formula (2) can be obtained by carrying out d+f mol addition of the ethyleneoxide to the polypropylene glycol which was made to carry out the e mol polymerization of the propylene oxide, and was obtained.

[0008] Moreover, when glycol system solvents, such as propylene glycol, ethylene glycol, and butanediol, are added to it, since the viscosity of polish liquid is lowered to the block-type polyether expressed with a general formula (1) and the dispersibility of moisture powder silicas, such as colloidal silica, is raised to it, it is still more desirable to it. When using together a block-type polyether and a glycol system solvent, it is desirable to make a glycol system solvent into 1 - 40 % of the weight to the constituent whole quantity 60 to 99% of the weight to the whole quantity of the constituent which consists a block-type polyether of a block-type polyether and a glycol system solvent.

[0009] The polish assistant for silicon wafers of above-mentioned this invention is usually added and used for the moisture powder silica which is an abrasive material. As a moisture powder silica, although a moisture powder powder silica, colloidal silica, etc. are mentioned for example, the alkaline colloidal silica adjusted to pH 8-12 especially is desirable. Also in alkaline colloidal silica, the 7-100-micrometer thing of mean particle diameter is desirable, and the concentration of alkaline colloidal silica has 20 - 60 desirable % of the weight.

[0010] Although especially the addition of the polish assistant for silicon wafers of this invention is not limited, it is desirable to add 0.005 to 5% of the weight to the solid content of a moisture powder silica. In addition, the silicon wafer polish assistant of this invention can be used together with surfactants, such as an alkylene oxide addition product of alkoxylate; higher alcohol of lower alcohol, such as lower alcohol; methyls cellosolve, such as a methanol, ethanol, and 2-propanol, ethylcellosolve, butyl cellosolve, methyl carbitol, ethyl carbitol, and butyl carbitol. Since the silicon wafer polish assistant of this invention can be used for either the wrapping process of a silicon wafer, or a polishing process and the surface tension of polish liquid can be adjusted to a suitable value, Hayes is not on a silicon wafer, a silicon wafer smooth [a front face] and flat can be obtained, and, as a result, the semiconductor device of high performance is obtained.

[0011]

[Example] Hereafter, an example explains this invention still more concretely. In addition, among the following examples, especially % is weight criteria, as long as it is unstated. The polish assistant and comparison article of this invention which were used for the evaluation trial are as follows.

[0012]

[Table 1]

表1

		ポリエーテル（A）			ポリエーテル（B）			ﾌﾟﾛﾋﾟﾚﾝｸﾞﾘｺｰﾙ (%)
		a＋c	b	配合量 (%)	a＋c	b	配合量 (%)	
本発明品	1	29	26	80	32	13	20	
	2	29	26	60	32	13	40	
	3	29	26	80	31	7	20	
	4	29	26	70	35	24	30	
	5	26	15	85	53	13	15	
	6	26	15	100				
	7	53	47	70	32	13	30	
	8	53	47	80	31	7	20	
	9	29	26	55	35	24	45	
	10	29	26	60	32	13	20	20
	11	17	15	70	32	13	30	

[0013]

[Table 2]

表2

		ポリエーテル（A）			ポリエーテル（C）			ﾌﾟﾛﾋﾟﾚﾝｸﾞﾘｺｰﾙ (%)
		a＋c	b	配合量 (%)	d＋f	e	配合量 (%)	
	12	29	26	70	9	34	30	
	13	32	13	20	33	37	60	20
	14	53	13	35	33	37	65	

[0014] * : in Table 1 and 2, a polyether (A) and (B) are block-type polyethers expressed with a general formula (1), and a polyether (C) is a block-type polyether expressed with a general formula (2).

[0015]

Comparison article 1 Sodium-aluminate comparison article 2 Lauryl sulfonic-acid sodium comparison article 3 Ten mol addition product comparison article 4 of nonyl phenol ethyleneoxides (blank)
[0016] (Example 1) This was diluted to 5.0% of silica solid content with water, using ADERAITO AT-30S (a trade name, the Asahi Denka Kogyo make, mean particle diameter of 7-10 micrometers, 30% of silica solid content) as colloidal silica. Addition of the polish assistant and comparison article of said this invention was carried out 0.1% (the comparison article 1 is 1.0%) to silica solid content, and to this, it stirred well, equalized to it, and considered as dilution polish liquid at it. These dilution polish liquid was used and wrapping processing was performed about 100 4 inches silicon wafers which carried out slicing. After wrapping processing, about the silicon wafer of 100 sheets, although it corresponded to each defect item of the abrasion of a wafer, the crack of a wafer, and the minute surface crack of a wafer, number of sheets was counted. The result is shown in Table 3.
[0017]
[Table 3]

表3

	擦り傷 (枚)	割れ (枚)	クラック (枚)
本発明品 1	0	0	0
本発明品 2	0	0	0
本発明品 3	1	0	0
本発明品 4	1	0	0
本発明品 5	1	0	0
本発明品 6	0	0	0
本発明品 7	0	0	0
本発明品 8	1	0	0
本発明品 9	0	0	0
本発明品10	1	0	0
本発明品11	1	0	0
本発明品12	1	0	0
本発明品13	1	0	0
本発明品14	1	0	0
比較例 1	5	5	4
比較例 2	6	4	3
比較例 3	3	5	4
比較例 4	9	10	10

[0018] (Example 2) This was diluted to 5.0% of silica solid content with water, using ADERAITO AT-30S (a trade name, the Asahi Denka Kogyo make, mean particle diameter of 7-10 micrometers, 30% of silica solid content) as colloidal silica. Addition of the polish assistant and comparison article of this invention was carried out 0.1% (the comparison article 1 is 1.0%) to silica solid content at this, and it stirred well, equalized and considered as dilution polish liquid. This dilution polish liquid was slushed into the polishing machine on condition that the following, and the primary polishing silicon wafer which passed through primary polishing processes was ground.
[0019] <Condition> polishing machine: LPH-15 amelioration machine (product made from a lap master)
polishing board diameter: -- 15 inch processing pressure force: -- 100g[/cm] 2 working temperature: -- 30-degree-C working liquid amount-of-supply: -- 10l. [/] hour floor-to-floor-time: -- 1-hour processing number-of-sheets: -- one-sheet polisher: -- SUPREME RN-H (the Rodel Nitta make)

Final polishing was performed under the above-mentioned conditions, after termination, it warned against drying a wafer front face, and RCA washing was carried out at 80 degrees C with hydrogen-peroxide-ammonia liquor. Quick discharge washing was performed after washing and it was made to dry with a spin dryer. The following evaluations were performed after desiccation.

[0020] Evaluation 1: The reflection from the wafer front face of halogen parallel light (super-high brightness checking lighting system U1 H-1 H, Intec make) was visually observed within the existence Green bench of Hayes, and generating of Hayes was observed.

Evaluation 2: Granularity was measured for the surface roughness of a surface roughness polish wafer the 2nd [an average of] power with the optical interference type granularity plan (WYKOTOPO-3D, the product made from WYKO, 250 micrometers).

Evaluation 3: The difference (TTV) of the surface display flatness of a display flatness polish wafer, i.e., the maximum thickness of a polish wafer, and the minimum thickness was measured with the TTV measuring device (the ADE micro scan 8300, product made from ADE).

Evaluation 4: 7x7 decreases of thickness of the wafer after grinding the polish rate of the silicon wafer under polish rate polish were measured, and were computed. These evaluation results are shown in Table 4.

[0021]

[Table 4]

表4

	ヘイズ	表面粗さ (nm)	平坦度 (μm)	研磨速度 (μm/分)
本発明品 1	無し	0.15	0.39	2.4
本発明品 2	無し	0.22	0.38	2.9
本発明品 3	無し	0.24	0.55	3.3
本発明品 4	無し	0.28	0.44	1.9
本発明品 5	無し	0.30	0.41	2.5
本発明品 6	無し	0.17	0.52	2.2
本発明品 7	無し	0.22	0.33	3.0
本発明品 8	無し	0.29	0.32	3.4
本発明品 9	無し	0.20	0.60	3.0
本発明品10	無し	0.27	0.30	2.9
本発明品11	無し	0.25	0.27	2.7
本発明品12	無し	0.31	0.51	2.8
本発明品13	無し	0.42	0.46	3.5
本発明品14	無し	0.30	0.45	2.9
比較例 1	無し	0.88	1.42	0.8
比較例 2	無し	0.91	1.33	0.7
比較例 3	無し	0.94	1.34	0.9
比較例 4	無し	1.24	2.04	1.4

[0022] Each evaluation result of the above example shows the polish liquid which used the polish assistant of this invention not having the crack or abrasion of a silicon wafer compared with the polish liquid which used the anionic surface active agent (comparison article 2) and the nonionic surface active agent (comparison article 3), and excelling in surface roughness, display flatness, a polish rate, etc.

[0023]

[Effect of the Invention] The effectiveness of this invention is to have offered the new silicon wafer polish assistant which gives the polish liquid which was more excellent in the polish engine performance.

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TECHNICAL FIELD

[Field of the Invention] This invention relates to the polish assistant for silicon wafers used suitable for mirror polishing of the silicon wafer in the production process of a semi-conductor.

[Translation done.]

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PRIOR ART

[Description of the Prior Art] There are a wrapping process (rough polish) which removes the cutting distorted layer and surface waviness which are produced when silicon is cut down in the shape of a wafer by cutting from a silicon ingot, and a polishing process (precision polish process) which makes the surface precision made into the purpose to lap DOSHIRIKONWEHA which passed through the wrapping process as mirror-polishing process of the silicon wafer for semi-conductors. Moreover, at the latter polishing process, it is classified by primary polishing processes (primary polish processes) to which a great portion of precision is made, and the final polishing process (the last polish process) to which the surface precision made into the purpose is made, and primary polishing processes may be called the primary secondary polishing processes by dividing into two depending on the case. Conventionally, generally as an abrasive material of a silicon wafer, colloidal silica and cerium oxide have been used. However, when it grinds only using colloidal silica polish liquid or cerium oxide polish liquid, there is a problem that Hayes (cloudiness) is generated on the surface of a silicon wafer, at the time of polish process termination. Moreover, when the powder-like silica was used as an abrasive material, it was hard to generate Hayes, but if the process which homogeneity is made to distribute was newly needed for a water solution and the powder-like silica was put further, in order that a powder-like silica might precipitate, polish liquid always needed to be stirred. Although the method of improving the silicon wafer abrasive material which used colloidal silica, and the polish approach was proposed by JP,2-125413,A, JP,61-209909,A, and JP,61-209910,A, the present condition was not being solution of a fundamental problem.

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EFFECT OF THE INVENTION

[Effect of the Invention] The effectiveness of this invention is to have offered the new silicon wafer polish assistant which gives the polish liquid which was more excellent in the polish engine performance.

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TECHNICAL PROBLEM

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MEANS

[Means for Solving the Problem] Then, this invention persons inquire wholeheartedly, and the polyether which has specific structure discovered that the engine performance superior to the conventional polish assistant was shown, and completed this invention. That is, this invention is the following general formula (1).
HO-(PO)a-(EO)b-(PO)c-H (1)
(-- EO expresses an oxyethylene radical among a formula, PO expresses an oxypropylene radical, and a, b, and c express one or more numbers.) -- it is the polish assistant for silicon wafers which consists of a block-type polyether expressed.
[0005]
[Embodiment of the Invention] In a general formula (1), EO expresses an oxyethylene radical and PO expresses an oxypropylene radical. a, b, and c express one or more numbers. Although the range of the desirable value of a, b, and c does not generally have ****** since it changes with molecular weight, HLB, etc. of a block-type polyether which are expressed with a general formula (1) interrelatively, a+c and b are usually ten to about 100 still more preferably two to about 500, respectively. The block-type polyether expressed with a general formula (1) can be obtained by carrying out a+c mol addition of the propylene oxide to the polyethylene glycol which was made to carry out the b mol polymerization of the ethyleneoxide, and was obtained. Under the present circumstances, since the physical properties of the block-type polyether obtained, for example, surface tension, a hydrophilic property, etc. are controllable by the molecular weight of the polyethylene glycol used as the base, the amount of propylene oxide made to add, it is possible to use it, choosing the block-type polyether suitable for the silicon wafer ground or the approach of grinding.
[0006] Moreover, although especially the molecular weight of the block-type polyether expressed with a general formula (1) is not limited, if the effectiveness of adjusting the surface tension of polish liquid if too not much small etc. becomes inadequate and is too large not much, since the viscosity of the block-type polyether expressed with a general formula (1) will rise too much, 1,000-10,000 are desirable. Two or more sorts of block-type polyethers from which the value of a, b, or c differs can be used as well as using one sort independently, and, as for the block-type polyether expressed with a general formula (1), it is desirable to use together and use two or more sorts to tune surface tension, a hydrophilic property, etc. of polish liquid finely. Especially the thing that gives desirable surface tension to the polish liquid which grinds a silicon wafer also in the block-type polyether expressed with a general formula (1) is a block-type polyether whose weight ratio of EO and PO is EO:PO=5:95-60:40. Since the surface tension which was suitable for polish liquid especially grinding a silicon wafer can be given when such a block-type polyether is used, there is not Hayes, a silicon wafer smooth [a polish front face] and flat can be obtained, and, as a result, the semiconductor device of high performance is obtained.
[0007] Furthermore, the block-type polyether expressed with a general formula (1) can be used together with the block-type polyether expressed with the following general formula (2).
HO-(EO)d-(PO)e-(EO)f-H (2)
In a general formula (2), d, e, and f express one or more numbers. Although the range of the desirable

value of d, e, and f does not generally have ****** since it changes with molecular weight, HLB, etc. of a block-type polyether which are expressed with a general formula (2) interrelatively, d+f and e are usually ten to about 100 still more preferably two to about 500, respectively. The block-type polyether expressed with a general formula (2) can be obtained by carrying out d+f mol addition of the ethyleneoxide to the polypropylene glycol which was made to carry out the e mol polymerization of the propylene oxide, and was obtained.

[0008] Moreover, when glycol system solvents, such as propylene glycol, ethylene glycol, and butanediol, are added to it, since the viscosity of polish liquid is lowered to the block-type polyether expressed with a general formula (1) and the dispersibility of moisture powder silicas, such as colloidal silica, is raised to it, it is still more desirable to it. When using together a block-type polyether and a glycol system solvent, it is desirable to make a glycol system solvent into 1 - 40 % of the weight to the constituent whole quantity 60 to 99% of the weight to the whole quantity of the constituent which consists a block-type polyether of a block-type polyether and a glycol system solvent.

[0009] The polish assistant for silicon wafers of above-mentioned this invention is usually added and used for the moisture powder silica which is an abrasive material. As a moisture powder silica, although a moisture powder powder silica, colloidal silica, etc. are mentioned for example, the alkaline colloidal silica adjusted to pH 8-12 especially is desirable. Also in alkaline colloidal silica, the 7-100-micrometer thing of mean particle diameter is desirable, and the concentration of alkaline colloidal silica has 20 - 60 desirable % of the weight.

[0010] Although especially the addition of the polish assistant for silicon wafers of this invention is not limited, it is desirable to add 0.005 to 5% of the weight to the solid content of a moisture powder silica. In addition, the silicon wafer polish assistant of this invention can be used together with surfactants, such as an alkylene oxide addition product of alkoxylate; higher alcohol of lower alcohol, such as lower alcohol; methyls cellosolve, such as a methanol, ethanol, and 2-propanol, ethylcellosolve, butyl cellosolve, methyl carbitol, ethyl carbitol, and butyl carbitol. Since the silicon wafer polish assistant of this invention can be used for either the wrapping process of a silicon wafer, or a polishing process and the surface tension of polish liquid can be adjusted to a suitable value, Hayes is not on a silicon wafer, a silicon wafer smooth [a front face] and flat can be obtained, and, as a result, the semiconductor device of high performance is obtained.

[Translation done.]

* NOTICES *

1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

EXAMPLE

[Example] Hereafter, an example explains this invention still more concretely. In addition, among the following examples, especially % is weight criteria, as long as it is unstated. The polish assistant and comparison article of this invention which were used for the evaluation trial are as follows.
[0012]
[Table 1]

表1

		ポリエーテル（A）			ポリエーテル（B）			プロピレングリコール (%)
		a＋c	b	配合量 (%)	a＋c	b	配合量 (%)	
本発明品	1	29	26	80	32	13	20	
	2	29	26	60	32	13	40	
	3	29	26	80	31	7	20	
	4	29	26	70	35	24	30	
	5	26	15	85	53	13	15	
	6	26	15	100				
	7	53	47	70	32	13	30	
	8	53	47	80	31	7	20	
	9	29	26	55	35	24	45	
	10	29	26	60	32	13	20	20
	11	17	15	70	32	13	30	

[0013]
[Table 2]

表2

		ポリエーテル（A）			ポリエーテル（C）			プロピレングリコール (%)
		a＋c	b	配合量 (%)	d＋f	e	配合量 (%)	
	12	29	26	70	9	34	30	
	13	32	13	20	33	37	60	20
	14	53	13	35	33	37	65	

[0014] * : in Table 1 and 2, a polyether (A) and (B) are block-type polyethers expressed with a general formula (1), and a polyether (C) is a block-type polyether expressed with a general formula (2).
[0015]
Comparison article 1 Sodium-aluminate comparison article 2 Lauryl sulfonic-acid sodium comparison article 3 Ten mol addition product comparison article 4 of nonyl phenol ethyleneoxides (blank)
[0016] (Example 1) This was diluted to 5.0% of silica solid content with water, using ADERAITO AT-30S (a trade name, the Asahi Denka Kogyo make, mean particle diameter of 7-10 micrometers, 30% of

silica solid content) as colloidal silica. Addition of the polish assistant and comparison article of said this invention was carried out 0.1% (the comparison article 1 is 1.0%) to silica solid content, and to this, it stirred well, equalized to it, and considered as dilution polish liquid at it. These dilution polish liquid was used and wrapping processing was performed about 100 4 inches silicon wafers which carried out slicing. After wrapping processing, about the silicon wafer of 100 sheets, although it corresponded to each defect item of the abrasion of a wafer, the crack of a wafer, and the minute surface crack of a wafer, number of sheets was counted. The result is shown in Table 3.

[0017]

[Table 3]

表3

	擦り傷 (枚)	割れ (枚)	クラック (枚)
本発明品 1	0	0	0
本発明品 2	0	0	0
本発明品 3	1	0	0
本発明品 4	1	0	0
本発明品 5	1	0	0
本発明品 6	0	0	0
本発明品 7	0	0	0
本発明品 8	1	0	0
本発明品 9	0	0	0
本発明品１０	1	0	0
本発明品１１	1	0	0
本発明品１２	1	0	0
本発明品１３	1	0	0
本発明品１４	1	0	0
比較例 1	5	5	4
比較例 2	6	4	3
比較例 3	3	5	4
比較例 4	9	１０	１０

[0018] (Example 2) This was diluted to 5.0% of silica solid content with water, using ADERAITO AT-30S (a trade name, the Asahi Denka Kogyo make, mean particle diameter of 7-10 micrometers, 30% of silica solid content) as colloidal silica. Addition of the polish assistant and comparison article of this invention was carried out 0.1% (the comparison article 1 is 1.0%) to silica solid content at this, and it stirred well, equalized and considered as dilution polish liquid. This dilution polish liquid was slushed into the polishing machine on condition that the following, and the primary polishing silicon wafer which passed through primary polishing processes was ground.

[0019] <Condition> polishing machine: LPH-15 amelioration machine (product made from a lap master)
polishing board diameter: -- 15 inch processing pressure force: -- 100g[/cm] 2 working temperature: -- 30-degree-C working liquid amount-of-supply: -- 10l. [/] hour floor-to-floor-time: -- 1-hour processing number-of-sheets: -- one-sheet polisher: -- SUPREME RN-H (the Rodel Nitta make)
Final polishing was performed under the above-mentioned conditions, after termination, it warned against drying a wafer front face, and RCA washing was carried out at 80 degrees C with hydrogen-peroxide-ammonia liquor. Quick discharge washing was performed after washing and it was made to dry with a spin dryer. The following evaluations were performed after desiccation.

[0020] Evaluation 1: The reflection from the wafer front face of halogen parallel light (super-high brightness checking lighting system U1 H-1 H, Intec make) was visually observed within the existence Green bench of Hayes, and generating of Hayes was observed.
Evaluation 2: Granularity was measured for the surface roughness of a surface roughness polish wafer the 2nd [an average of] power with the optical interference type granularity plan (WYKOTOPO-3D, the product made from WYKO, 250 micrometers).
Evaluation 3: The difference (TTV) of the surface display flatness of a display flatness polish wafer, i.e., the maximum thickness of a polish wafer, and the minimum thickness was measured with the TTV measuring device (the ADE micro scan 8300, product made from ADE).
Evaluation 4: 7x7 decreases of thickness of the wafer after grinding the polish rate of the silicon wafer under polish rate polish were measured, and were computed. These evaluation results are shown in Table 4.
[0021]
[Table 4]

表4

	ヘイズ	表面粗さ (nm)	平坦度 (μm)	研磨速度 (μm/分)
本発明品 1	無し	0.15	0.39	2.4
本発明品 2	無し	0.22	0.38	2.9
本発明品 3	無し	0.24	0.55	3.3
本発明品 4	無し	0.28	0.44	1.9
本発明品 5	無し	0.30	0.41	2.5
本発明品 6	無し	0.17	0.52	2.2
本発明品 7	無し	0.22	0.33	3.0
本発明品 8	無し	0.29	0.32	3.4
本発明品 9	無し	0.20	0.60	3.0
本発明品10	無し	0.27	0.30	2.9
本発明品11	無し	0.25	0.27	2.7
本発明品12	無し	0.31	0.51	2.8
本発明品13	無し	0.42	0.46	3.5
本発明品14	無し	0.30	0.45	2.9
比較例 1	無し	0.88	1.42	0.8
比較例 2	無し	0.91	1.33	0.7
比較例 3	無し	0.94	1.34	0.9
比較例 4	無し	1.24	2.04	1.4

[0022] Each evaluation result of the above example shows the polish liquid which used the polish assistant of this invention not having the crack or abrasion of a silicon wafer compared with the polish liquid which used the anionic surface active agent (comparison article 2) and the nonionic surface active agent (comparison article 3), and excelling in surface roughness, display flatness, a polish rate, etc.

[Translation done.]